The dissociative adsorption of hydrogen: Two-, three-, and four-dimensional quantum simulations

Nielsen, Ulrik; Halstead, David; Holloway, Stephen; Nørskov, Jens Kehlet

Published in:
Journal of Chemical Physics

Link to article, DOI:
10.1063/1.458873

Publication date:
1990

Document Version
Publisher's PDF, also known as Version of record

The dissociative adsorption of hydrogen: Two-, three-, and four-dimensional quantum simulations

Ulrik Nielsen
Institute of Physics, University of Aarhus, DK 8000 Aarhus C, Denmark

David Halstead and Stephen Holloway
Surface Science Research Centre, University of Liverpool, P.O. Box 147, Liverpool L69 3BX, United Kingdom

J. K. Nørskov
Laboratory of Applied Physics, Technical University of Denmark, DK 2800 Lyngby, Denmark and, Haldor Topsøe Research Laboratories, Nymøllevej, DK 2100 Lyngby, Denmark

(Received 14 March 1990; accepted 11 May 1990)

A quantum wave packet calculation for the activated dissociative adsorption of H_2 is presented. Restricting the motion of the molecule to lie within a plane normal to the surface we have treated all four molecular degrees of freedom exactly. We compare results obtained using two-, three-, and four-dimensional simulations on the same potential and show that by restricting the molecular orientation, important dynamical effects are lost. The potential employed in the calculations has been obtained using the effective medium approximation. In the simulations it has been possible to treat dissociation, rotations and diffraction on an equal footing. By including a rotational degree of freedom, it is seen that strong orientational effects occur near to the transition state and result in an anisotropic selectivity in the dissociation. By examining the state-to-state scattering probabilities, it is possible to use the nonreacting (scattered) fraction to provide information on the reactive potential energy surface.

I. INTRODUCTION

Within the past few years, there have been a number of theoretical papers dealing with the dissociation of diatomic molecules on surfaces exhibiting an activation barrier.[1-7] Because of the quantum nature of the problem, wave packet methods have been used to solve for the time dependence of the interacting system. Due to computational restrictions, however, such calculations have imposed rather severe limitations on the allowed geometry taken by the molecule, which is frequently oriented with its molecular axis parallel to the surface.[5-7] While results have afforded insight into the general process of molecular dissociation, it is of fundamental interest to ascertain how the six molecular degrees of freedom are coupled together at the transition state.

In this paper we compare results for two-, three-, and four-dimensional quantum simulations for a H_2 molecule interacting with a metal surface. In order to facilitate such a comparison it is necessary to (i) obtain a realistic potential energy hypersurface (PES) capable of supporting the additional dimensionality, and (ii) be able to perform the time dependent quantum simulation. Both these criteria have been met by employing an effective medium potential for H_2 on a Cu surface[8] and using the split operator method for wave packet propagation.[9]

The principal conclusions arising from the present 2-D calculations are in general accord with those found in previous works.[5-7] There is considerable coupling between vibrational and translational motion in the reaction zone of the PES and in addition, a certain fraction of the dissociated molecules tunnel through the barrier. Gratifyingly, some of these effects remain in the higher dimensionality calculations, a fact which gives some credibility to studying the (cheaper) 2-D and 3-D systems. The 4-D simulations show that there is strong dynamical mixing between the rotational and vibrational degrees of freedom that is totally excluded from simulations of lower dimensionality. This may be understood in terms of a simple ansatz rotational wave function for the scattered flux which is derived under the assumption that the dissociation probability depends markedly upon the orientation of the molecule with respect to the surface.[10] Moreover, it is possible that by inverting the rotational scattering probabilities, important information may be obtained concerning the topology of the PES near the transition state.

In the following section, a brief description of the potential energy surface and the wave packet propagation method are given. Section III contains the results of the quantum wave packet simulations. Finally a discussion is presented where the main conclusions are given.

II. CALCULATIONAL DETAILS

Restricting the molecule to lie in a plane perpendicular to the metal surface, parallel to a high symmetry direction in the surface, we explicitly treat the motion of each proton independently. While this does not imply that azimuthal angle (ϕ) effects for dissociation will be negligible or even uninteresting, there will be stronger dynamical effects for variations in the polar angle (θ) which is included in the calculation; dissociation cannot occur for a molecule constrained to have its axis normal to the surface ($\theta = 0$) and impulsive collisions will predominantly excite cartwheel ro-

 0021-9606/90/162879-06$03.00

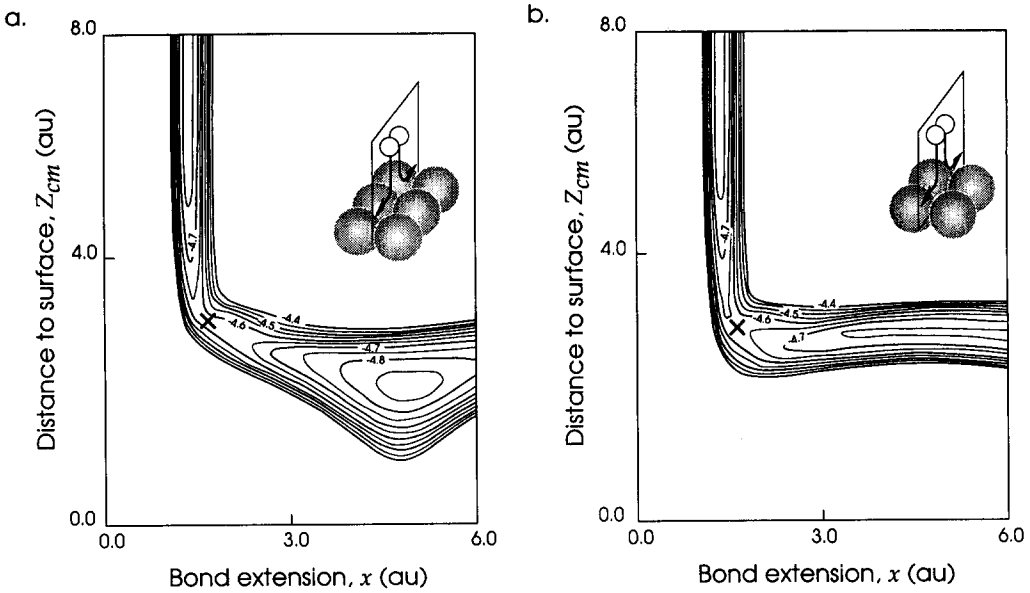

FIG. 1. Two cuts of the potential energy surface used in this study. Both are for the restricted geometry that keeps the molecular axis parallel to the surface. Contour values are in eV and the zero of energy is taken to be two dissociated hydrogen atoms far from the surface. On this scale the well depth of the gas-phase H_2 molecule is -4.79 eV. (a) Shows the bridge-to-center slice. The location of the activation barrier is shown by a cross and its value is $E_{act} \sim 175$ meV. (b) Is for the center-to-bridge dissociation and clearly shows the sharp turn that the wave packet must make in order that the molecule may dissociate. Even though the activation barrier is somewhat lower than for the bridge-to-center cut ($E_{act} \sim 155$ meV), the sharp corner in the reaction zone hinders the dissociation to an extent that the 2-D sticking coefficient appears very similar for both surfaces (see Fig. 2).

tations with **J** parallel to the surface.[11] The two protons are located at X_1, Z_1 and X_2, Z_2, where X is in the plane and Z is normal to the surface. For propagation, a second choice of coordinates is employed which refers to the center of mass $X_{cm} = (X_1 + X_2)/2$ and $Z_{cm} = (Z_1 + Z_2)/2$ and the relative atomic separations $x = X_1 - X_2$ and $z = Z_1 - Z_2$.

The potential chosen has been derived within the effective medium approximation and simulates the interaction of H_2 with a Cu(100) surface.[8] The scattering plane is defined by the ⟨110⟩ direction containing the center and bridge sites. Topologically, the potential energy surface obtained by fixing $Z_1 = Z_2$ and $X_1 = -X_2$ (the commonly seen "elbow" plot) contains an activation barrier with magnitude $E_{act} \sim 165$ meV which is located midway along the reaction path separating the gas-phase and the dissociated species. There is a 20 meV difference between the value of E_{act} at the bridge and center site, the minimum barrier being found at the former position. This is shown in detail in Fig. 1. No total energy calculation for dissociative adsorption has yet produced an activation energy of an accuracy good enough to make direct comparison with experiment. The finding that H_2 adsorption on Cu(100) is activated is in agreement with experiment, but the calculated barrier appears too low. In this work we are using the PES to compare different dimensionality calculations rather than attempt a detailed comparison with experimental data, for this purpose the present PES should be well suited. In general, it represents a particular *class* of systems having a barrier which is low when compared to the $0 \rightarrow 1$ vibrational excitation in the free molecule.[12] For a detailed description of the PES construction the interested reader is referred to the paper by Nørskov.[8] Since the transition state is not located in the entrance channel, the potential energy surface has a topology that will serve to reduce the perceived activation barrier.[12] This occurs because of the interconversion of the molecular vibrational (zero point or otherwise) and translational energies as the reaction path is traversed.

To solve for the quantum dynamics, the split operator method of Fleck, Morris and Feit has been used[9] the application of which, to surface scattering problems, has been extensively discussed elsewhere.[4,5,7] Using the four coordinates X_{cm}, Z_{cm}, x and z, the mapping of the split operator propagation scheme becomes trivial, the details of which will be presented elsewhere.[13] The number of mesh points required to resolve each dimension and the various box lengths are presented in Table I. An absorbing boundary was placed in the outermost 16 points along each edge of the x coordinate to deal with flux lost through surface mediated dissociation. No boundary is needed in the z coordinate since for this dimension the potential rises steeply towards the box edges. Furthermore, significant amplitude in this region would physically correspond to desorption of a single atom, a pro-

TABLE I. Grid parameters used in the calculation.

Coordinate (au)	Grid size (points)
$-6.0 < x < +6.0$	128
$-3.0 < z < +3.0$	32
$-2.33 < X_{cm} < +2.33$	8
$-0.5 < Z_{cm} < +17.5$	128

cess which is forbidden for the energies used in this work.

The initial state is chosen to be that of a beam of molecules incident normally to the surface in the ground rotational and vibrational states,

$$\psi_i \sim \phi_0(r) g(Z_{cm} - Z^i_{cm}, k^i_Z). \quad (1)$$

$g(Z,k^i_Z)$ is a Gaussian wave packet with momentum k^i_Z and $\phi_0(r)$ is a vibrationally ground state wave function evaluated at $Z_{cm} \to \infty$, where $r = \sqrt{x^2 + z^2}$. Since the wave function is found for each time increment, the projection onto asymptotic final states is relatively straightforward. The excitations of interest are molecular rotation, diffraction and dissociation. No vibrational excitation can occur for the scattered flux as the translational energies used in this work lie well below the 512 meV threshold for the $0 \to 1$ transition in gas-phase H_2. Consequently, as far as the scattered flux is concerned, the collision is vibrationally adiabatic. The final state scattered wave function is given by

$$\psi_f(r,\theta,X_{cm},Z_{cm}) = \sum_{j,n} a^j_n \Psi^j_n(r,\theta,X_{cm},Z_{cm}), \quad (2)$$

where

$$\Psi^j_n(r,\theta,X_{cm},Z_{cm}) = S^j_n \exp(ij\theta)\exp(ig_n X_{cm}) \times h(Z_{cm} - Z^f_{cm}, k^f_Z)\phi_0(r), \quad (3)$$

and the differential scattering intensities are simply

$$I^j_n = |a^j_n|^2. \quad (4)$$

$h(Z,k^i_Z)$ is a localized function (not necessarily a Gaussian), S^j_n is a normalization constant, j the rotational quantum number, g_n is the nth reciprocal lattice vector and the final momentum in the Z_{cm} direction simply conserves total energy

$$\frac{k^{f^2}_Z}{2M} + \frac{j^2}{2I} + \frac{g^2_n}{2M} = \frac{k^{i^2}_Z}{2M}. \quad (5)$$

Results presented in the next section are for the $0 \to n$ diffracted intensities and the $0 \to j$ rotational excitation probabilities. Since the calculations obey unitarity, by summing $|a^j_n|^2$ over both j and n it is possible to obtain a value for the number of particles that dissociatively adsorb on the surface. We associate these particles with the sticking fraction, S_0.

III. RESULTS

Figure 2 shows S_0 as a function of the initial translational energy E_i. Results for several calculations are shown for varying degrees of dimensionality. The 2-D calculations are for sections defined by restricting $Z_1 = Z_2$ and $X_1 = -X_2$ and correspond to the usual geometry adopted

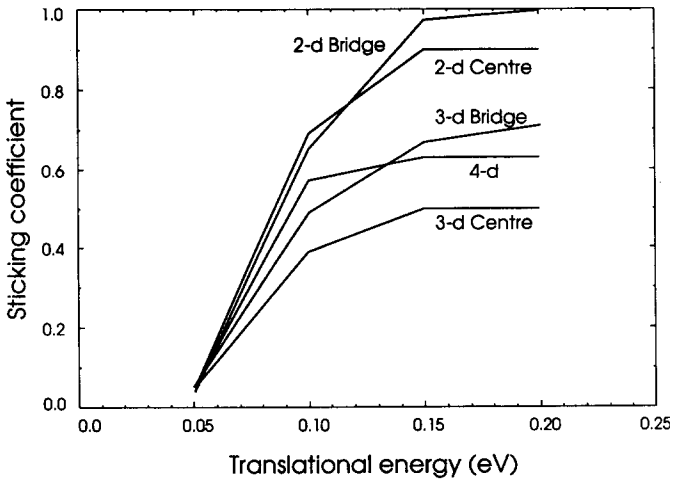

FIG. 2. The sticking coefficient as a function of translational energy of the molecule. Shown in this figure are the 2-D results for a dissociation geometry which restricts the molecular axis to be parallel with the surface and the center of mass to be either above a bridge site or a center site (see Fig. 1). Additionally 3-D results are shown whereby the center of mass is constrained to be either over the center or bridge. In these cases the molecule can undergo "cartwheel" rotations in a plane. Finally, results for a 4-D calculation are given where, in addition to the 3-D simulations, we allow the center of mass to translate within the plane of rotation. The results show that by including the rotational degree of freedom, the dissociation probability at high energies saturates at a value significantly less than unity. This is because those molecules aligned with their axis parallel to the surface normal, have an unfavorable dissociation geometry, and are scattered into the gas-phase.

in such simulations where the molecule has its axis parallel to the surface. The two curves shown are for impact parameters corresponding to the bridge and center sites (Fig. 1). The onset of dissociation is far below the value of the activation barrier ~ 165 meV for either site. This effect has been seen on several previous occasions and has its origins in two effects (i) vibrational to translational energy transfer ($V \to T$) as the molecule traverses the "corner" of the reaction zone, and (ii) tunneling through the activation barrier. Both curves rise rather steeply, indicating a narrow barrier, and saturate near $E_i \sim 170$ meV with the bridge simulation levelling near unity sticking probability and the center simulation at 0.9. What this implies is that there is very little difference between the *dynamics* at the two sites in the surface. Looking at the immediate contrast between the two plots shown in Fig. 1 this may seem surprising. However, while the barrier at the center site is certainly less than that at the bridge site, in order to dissociate at the center, the molecule must make a very sharp turn which results in unfavorable dissociation dynamics. This is exactly the opposite to what occurs at the bridge site where the dissociating molecule simply runs down in the direction of the chemisorption minimum, located above the center site. At the highest values of E_i the sharp turn required at the center site cannot be made, since the turn around time in Z_{cm} is too quick and hence the saturation value never reaches unity. These results should be contrasted with those for the full 4-D calculation

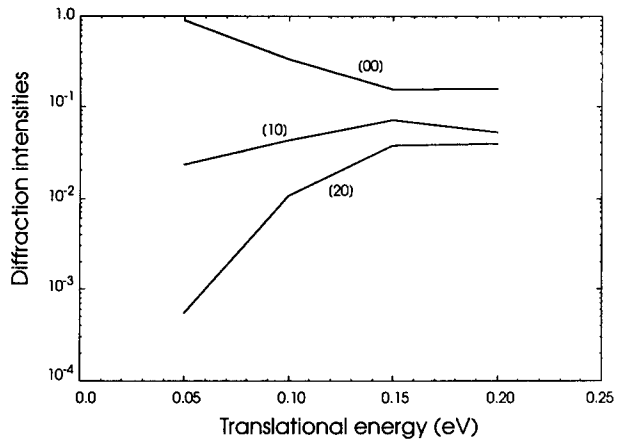

FIG. 3. The diffracted intensities as a function of initial translational energy obtained from the 4-D calculation.

shown in the same figure. While the onset of dissociation occurs at approximately the same value as in the 2-D calculation, the saturation value of S_0 is only 0.6! The reasons for this difference can only lie in changes brought about either by rotational or X_{cm} translational coupling. Since it has been seen that differences in the dynamics between the two sites is a weak factor, we conclude that the rotational coupling at the transition state accounts for this strong suppression in S_0. To probe this in more detail we have performed 3-D calculations where we restrict the molecular motion to have its center of mass fixed over either the center or bridge sites. The results for the dissociation, also shown in Fig. 2, are

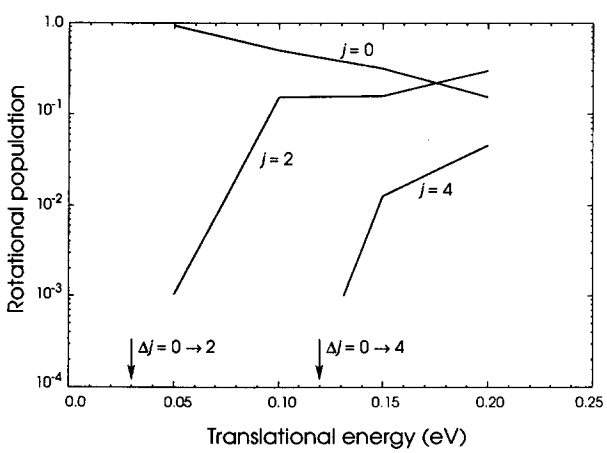

FIG. 4. The rotational excitation probabilities for the 3-D calculation described in the text. This occurs as a consequence of the stereospecificity in the dissociation process. Those molecules with their molecular axis parallel to the surface normal do not dissociate and as a consequence, the scattered flux has lost a particular angular fraction [see Eq. (7)]. Translated into a final state distribution, this implies rotational excitation. Alternatively one can think of this as arising from a strongly anisotropic gas-surface potential. The thresholds for the first two rotational excitations are indicated by arrows.

enlightening. Now the saturation values for S_0 are 0.5 and 0.7, respectively. It can therefore be concluded that the diminished asymptotic sticking coefficient is principally due to rotational effects and not to variation in the dissociation probability across the unit cell.

Figure 3 shows the diffraction intensities for the full 4-D calculation obtained by summing over the rotational satellites

$$P_n = \sum_j |a_n^j|^2. \tag{6}$$

As the translational energy approaches zero, all of the intensity is in the (00) beam since the Bragg condition for diffraction cannot be satisfied. As E_i increases, the higher order diffraction states begin to get populated, with thresholds at 6.7 meV ($0\rightarrow 1$) and 26.8 meV ($0\rightarrow 2$). These results are in good agreement with those obtained from a 2-D calculation (in X_{cm} and Z_{cm}) performed on a similar potential energy surface by Halstead and Holloway.[4] Essentially as the fraction of the unit cell supporting dissociation begins to open, the diffracted intensities grow in and it is only at the highest energies, when S_0 plateaus, that the situation begins to stabilize. Again it should be mentioned that *as the barrier to dissociation opens, nothing particularly drastic happens to the diffracted intensities* as was found in the previous work.[4]

In order to investigate the strong rotational effects seen above, Fig. 4 shows the rotational excitation probability for the 3-D calculation where the H_2 is constrained to be above the center site. For $j\neq 0$, probabilities have been doubled to account for the degeneracy of $+j$ and $-j$ states. The selection rule on Δj is restricted to ± 2 since we have a homonuclear diatomic. The results clearly show that as dissociation begins, there is a dramatic increase in the amount of rotational excitation. The thresholds for rotational excitation are 30 meV ($0\rightarrow 2$) and 120 meV ($0\rightarrow 4$). In order to get a baseline for H_2 scattering, typically in the absence of dissociation, less than $\sim 10\%$ would be expected in j states other than zero.[14–16] It would appear, therefore, that the observation of rotationally excited scattered molecules would be a good indication that dissociation is occurring. The reason for this is linked to the strong anisotropy in the potential energy surface near to the transition state and will be discussed in the following section.

IV. DISCUSSION AND CONCLUSIONS

The single most important aspect emerging from these calculations has been the strong coupling between vibrational and rotational energy that occurs in the reactive region of the PES. Calculations that restrict the bond axis to be parallel to the surface, most certainly miss an important part of the dynamical behavior. For the particular PES chosen for these calculations, there were no strong effects due to the center of mass impact parameter. As a consequence, the diffraction features obtained did not contain enough information to allow a determination of the activation barrier position within the unit cell. It has previously been shown[4] that when there is a significant variation in E_{act} across the surface, the diffraction intensities can give important information regarding the spatial location of the transition state.

The rotational distributions contain far more excitations than would be generated from a simple impulsive collision.[16] To understand this effect it is necessary to consider the distribution (in θ-space) of the final state wave function. The initial distribution is simply uniform, representative of a beam in the $j=0$ state and the occurrence of strong rotational scattering implies that this symmetry is broken. The dominant mechanism that will give rise to a nonuniform sampling in θ-space is the dissociation process itself which will have a strong angular dependence. This arises in its most naïve form from the fact that molecules having their bond axis parallel to the surface will dissociate more readily than those oriented perpendicular.[17] Therefore, the act of dissociation serves as a form of angular filter and selectively removes from the scattered flux those molecules arriving broadside to the surface. To illustrate this point consider as an ansatz for the scattered rotational wave function[10]

$$\psi_f = \frac{1}{\sqrt{2\pi}}\left[1 - A\left\{\exp\left(-\left[\frac{\theta-\pi/2}{\alpha}\right]^2\right) + \exp\left(-\left[\frac{\theta-3\pi/2}{\alpha}\right]^2\right)\right\}\right], \quad (7)$$

which corresponds to the incident rotational state minus two Gaussian shaped portions which we assume have contributed to the dissociated fraction. In the limit of $\alpha < 90°$ the sticking coefficient is readily evaluated to be

$$S_0 \sim \frac{A\alpha}{\sqrt{2\pi}}\left[2\sqrt{2} - A\right]. \quad (8)$$

The scattered rotational probabilities are obtained by projecting Eq. (7) onto the wave functions $\exp(ij\theta)/\sqrt{2\pi}$ giving[10]

$$|P_0|^2 = \left[1 - \frac{A\alpha}{\sqrt{\pi}}\right],$$

and

$$|P_j|^2 = \frac{(A\alpha)^2}{2\pi}\exp\left(-\frac{j^2\alpha^2}{2}\right)\left[1+\cos(j\pi)\right] \quad (j\neq 0), \quad (9)$$

where we have chosen the distributions to be normalized to $(1-S_0)$. Using this simple argument it is clear that rotational excitation in the scattered flux will occur as a direct consequence of θ-anisotropy in the PES, the magnitude of which is related to the angular tolerance in the dissociation probability. It is possible to obtain an approximate value for A by equating it to the value of S_0 found in the 2-D calculations. For $A=0.5$ ($E_i = 0.09$ eV) and 0.9 ($E_i = 0.15$ eV), the values of α which give the correct sticking fraction in the 4-D calculation [Eq. (8)] are $\sim 60°$ and 70°, respectively. For these parameter values the rotational populations from Eq. (9) are $|P_0|^2 \sim 50\%$ and $|P_2|^2 \sim 2\%$ at 0.09 eV and $|P_0|^2 \sim 7\%$ and $|P_2|^2 \sim 4\%$ at 0.15 eV. These numbers compare favorably with the "exact" values shown in Fig. 4.

It has therefore been shown that while extending the dimensionality of the dissociative adsorption calculations substantiates some of the previous assertions based on 2-D models, new physical features arise which cannot be ignored. There is still significant $V \rightarrow T$ energy transfer as the molecule "turns the corner" *en route* to dissociation, resulting in an effective activation barrier [i.e., as found in an $S_0(E_i)$ plot] which is significantly lower than the value read off from the potential energy surface.[12] This is an important result since when attempting to synthesize potentials from spectroscopic data, it is common to associate potential energy values to experimentally observed well depths and barrier heights. In systems exhibiting strong coupling between several degrees of freedom this procedure is highly questionable and frequently misleading.[18] As in the 2-D calculations, tunnelling of the molecule occurs in the vibrational coordinate.[19] There is little evidence that the molecule finds it any more torturous to tunnel than be rotationally realigned and scatter from the surface. For this to happen there would have to be significantly large steering forces in the attractive well, a feature absent in the PES used here and for most that have been employed in studies of H_2 adsorption.[2-5,7] There is a relatively large measure of rotational excitation in the scattered molecules which does not appear to be related to simple "mechanical" excitation.[16] Instead we believe this to occur as a consequence of the strong dependence of the dissociation probability on the molecular orientation. On the basis that those molecules having their axis normal to the surface will survive intact and those lying flat will not, a simple model has been described[10] that accounts for the large rotational excitation probabilities observed in the quantum simulations.

Comparing the results shown in Fig. 2 with recent experimental data for the dissociation probabilities of H_2 from Cu surfaces[20,21] would indicate that the PES employed in this calculation underestimates the magnitude of the activation barrier. While this may indeed be true, we do not believe that this affects the major conclusions drawn in this work which concerns the issue of the dimensionality of the quantum simulation.

Regarding the question of inverting the scattering data to provide information on the reactive PES, the calculations offer two possibilities. As was noted previously,[4] studying the molecular diffraction intensities as dissociation occurs could give possible clues to the location of the activation barrier position within the unit cell of the surface. This technique can be significantly enhanced if D_2 as well as H_2 is used as a probe. Secondly, by measuring the rotational probability distributions, it should be possible to gain information on the stereospecificity of the dissociation process. This is valuable information which, to our knowledge, cannot be determined in any other way for homonuclear diatomics. Further, measuring the alignment and orientation moments[22] of the scattered flux should enable even stronger constraints to be placed upon possible potential energy surfaces.

ACKNOWLEDGMENTS

The authors acknowledge valuable discussions with Bret Jackson and Stig Andersson. This work was funded in part by an EEC twinning grant No. ST2J-0286-C(TT).

[1] A. Gelb and M. Cardillo, Surf. Sci. **59**, 128 (1976); **64**, 197 (1977); **75**, 199 (1978).
[2] A. E. DePristo and A. Kara, Adv. Chem. Phys. (in press).
[3] M. Karikorpi, S. Holloway, N. Henriksen, and J. K. Nørskov, Surf. Sci. **179**, L41 (1987).

[4] D. Halstead and S. Holloway, J. Chem. Phys. **88**, 7197 (1988).
[5] B. Jackson and H. Metiu, J. Chem. Phys. **86**, 1026 (1987).
[6] M. Asscher, O. M. Becker, G. Haase, and R. Kosloff, Surf. Sci. **206**, L880 (1988); J. Chem. Phys. **90**, 3346 (1989).
[7] M. Hand and S. Holloway, Surf. Sci. **211/212**, 940 (1989); J. Phys.: Condens. Matter **1**, SB27 (1989); J. Chem. Phys. **91**, 7209 (1989).
[8] J. K. Nørskov, J. Chem. Phys. **90**, 7461 (1989).
[9] J. A. Fleck Jr., J. R. Morris, and M. D. Feit, Appl. Phys. **10**, 129 (1976).
[10] S. Holloway and B. Jackson, Chem. Phys. Lett. (to be published).
[11] G. Sitz, A. Kummel, and R. N. Zare, J. Vac. Sci. Technol. **A5**, 513 (1987).
[12] D. Halstead and S. Holloway, J. Chem. Phys. (to be published).
[13] U. Nielsen (to be published).
[14] J. Lapujoulade and J. Perreau, Phys. Scr. **T4**, 138 (1983).
[15] J. Harris, S. Andersson, C. Holmberg, and P. Nordlander, Phys. Scr. **T13**, 155 (1986).
[16] R. C. Mowrey, Y. Sun, and D. J. Kouri, J. Chem. Phys. **91**, 6519 (1989).
[17] P. K. Johansson, Surf. Sci. **104**, 510 (1981).
[18] A. V. Hamza and R. J. Madix, J. Phys. Chem. **89**, 5381 (1985).
[19] S. Holloway, A. Hodgson, and D. Halstead, Chem. Phys. Lett. **147**, 425 (1988).
[20] G. Anger, A. Winkler, and K. D. Rendulic, Surf. Sci. **220**, 1 (1989).
[21] B. E. Hayden and C. L. A. Lamont, Chem. Phys. Lett. **160**, 331 (1989); Phys. Rev. Lett. **63**, 1823 (1989).
[22] X. Y. Chang and S. Holloway (to be published).